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A Fire Risk Assessment for Bio Ethyl *Tert*-Butyl Ether (ETBE)

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Abstract

The present article deals with a fire risk assessment for bio ethyl *tert*-butyl ether (ETBE). The fire risk has been assessed based on the heat release rate (HRR) and the carbon monoxide (CO) yield, using a cone calorimeter in accordance to testing procedure documented in ISO 5660-1:2002, which has been modified in order to enable the testing of flammable liquids. The research focuses on bio-ETBE used as bio component in automobile petrol (analytically pure ETBE was not a subject of this research). The sample weight used for a single testing was 100g at 745.1 kg.m^{-3} density. The sample was ignited with a spark igniter, avoiding additional heat radiation effect from the cone emitter. The following values were measured under the testing conditions: maximum HRR (2796 kW.m^{-2}), average HRR 876 kW.m^{-2}, average specific mass loss rate (SMLR) 23.08 g.m^{-2}.s^{-1} and the CO yield 10 g.kg^{-1}. Equations for the statistical dependence of HRR and specific CO production rate (SCPR) on SMLR were compiled from the obtained values. Further, the SMLR for ETBE burning in an infinite size pool 165.42 g.m^{-2}.s^{-1} was calculated. Substituting the calculated SMLR values (for pool fire in an infinite size pool) into the statistical dependence equations, HRR 6356 kW.m^{-2} and SCPR 2.57 g.m^{-2}.s^{-1} were calculated for pool ETBE fire under realistic conditions (pool diameter exceeding 3.5m). The calculated SCPR accounted for a CO yield of 15.54 g.kg^{-1}.

Keywords: Bio ethyl *tert*-butyl ether; cone calorimeter; fire investigation; fire risk; heat release rate; occupational safety and health; pool fire

1. Introduction

The 2003/30/EC European Parliament and Council Directive requires of member states that, commencing 31. December 2010, the energy proportion of biofuels and other renewable fuels in all petrol and diesel for transport purposes reaches a minimum of 5.75%. Bio-ETBE (ethyl-*tert*-butyl-ether), produced on the basis of bio ethanol, is among fuels regularly added to automobile petrol. Therefore, recent years have seen a significant increase in the

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amounts of ETBE present in chemical and petrochemical industries. Despite that, according to [1-3], fire is involved in approximately 40% of accidents in chemical industries and pool fire is more frequent than other types of fire, not all experimental data necessary for the assessment of ETBE fire hazard is currently available.

Nomenclature

D	pool diameter (m)
ETBE	ethyl *tert*-butyl ether (-)
HRR	heat release rate ($kW.m^{-2}$)
k	absorption-extinction coefficient (m^{-1})
$m^{''}$	specific mass loss rate for pool diameter D ($g.m^{-2}.s^{-1}$)
$m^{''}_{\infty}$	specific mass loss rate for infinite size pool ($g.m^{-2}.s^{-1}$)
SCPR	specific CO production rate ($g.m^{-2}.s^{-1}$)
β	mean-beam-length corrector (-)

The fire risk of a given material can be most exactly evaluated on the basis of the heat release rate (HRR) [4] and the yield of carbon monoxide (CO) [5]. A HRR of material is directly proportional to the heat of combustion, mass loss rate, and combustion efficiency. Effective heat of combustion is a material constant. In contrast, the mass loss rate, combustion efficiency, and the CO yield depend primarily on the oxidation atmosphere properties (its temperature, flow direction and speed, and oxygen concentration) and the density of the external heat flow affecting the surface of the burning material [6]. The influence of the oxidation atmosphere properties and of the external heat flow density on the ignition and burning process of organic matter and on the CO yield has been studied in detail byTewarson et al. [7], Ladomersky et al. [8], Zachar et al. [9],Pitel et al. [10],Mulliqi et al. [11], Roslyakov et al. [12], Chrebet et al. [13] and Martinka et al. [14-15]. In pool fires, the pool parameters (its diameter, the thermal-technical properties of the material, the depth level of liquid below the upper edge, and the ratio of diameter to height) have a significant influence on the specific mass loss rate (SMLR), the combustion efficiency and the CO yield.

The SMLR of flammable liquids (excluding alcohols) burning in a pool with a diameter of more than 0.2 m can be calculated according to equation (1), derived by Zabetakis and Burgess [16-19]. However, the research results by Martinka et al. [6] have shown that, when substituting the average SMLR, measured in intervals of 30 to 90 seconds from the start of testing in a cone calorimeter, the equation (1) also shows high accuracy in the calculation of SMLR for flammable liquids burning (during a cone calorimeter test) in a pool with a diameter of 0.106 m.

$$m^{''} = m^{''}_{\infty} \cdot (1 - \mathrm{e}^{-k \cdot \beta \cdot D}) \tag{1}$$

Where: $m^{''}$ is SMLR for pool diameter D ($kg.m^{-2}.s^{-1}$), $m^{''}_{\infty}$ is SMLR for infinite size pools ($g.m^{-2}.s^{-1}$), e is Euler´s number (-), k is absorption-extinction coefficient (m^{-1}), β is mean-beam-length corrector (-), and D is pool diameter (m) [16-19].

The SMLR of most flammable liquids (excluding alcohol) increases with an increasing pool diameter (from a diameter of 0.2 m). Starting at a diameter of 2 m, the SMLR of most flammable liquids is nearly constant (asymptotically approaching the infinite size pool value). Therefore, the SMLR, HRR, and CO yield data converted to an infinite pool size match real flammable liquid pool fire.

The aim of the present paper is to assess the fire risk of ethyl *tert*-butyl ether (ETBE). The fire risk has been assessed based on the HRR, SMLR, and CO yield values, using a cone calorimeter. The measured values have been converted for an infinite pool diameter.

2. Experiment description

The HRR, SMLR and CO yield for ETBE have been set on a cone calorimeter according to ISO 5660-1:2002 [20] with a modified testing procedure. The testing procedure modification included the utilisation of a cylindrical container with a diameter of 106 mm and a height of 15 mm (enabling the testing of flammable liquids in a cone calorimeter). The testing procedure was further modified by removing the cone emitter from the cone calorimeter (the sample was ignited using only a spark igniter, avoiding additional heat radiation effect during the ignition as well as the entire test duration). The utilised investigation procedure is described in detail by Martinka et al. [6].

An ETBE sample with a weight of 100 ± 1 g was used for each measurement. The measurement was repeated 5 times and the resulting average values are provided. The initial sample temperature was 20 °C. Table 1 shows the physical and chemical properties of the investigated ETBE.

Table 1.Physical and chemical properties of investigated ETBE [21].

Physical and chemical properties	
Density at 15 °C ($kg.m^{-3}$)	745.1
Ethyl *tert*-butyl ether content (% weight)	91.09
Methyl *tert*-butyl ether content (% weight)	0.04
Ethanol content (% weight)	1.48
Dimers content (% weight)	3.25
Tert-butanol content (% weight)	1.8
C4 hydrocarbons content (% weight)	0.2
C5 and higher hydrocarbons content (% weight)	1.94

3. Results and discussion

The HRR and SMLR of the investigated ETBE are shown in Fig.1. The maximum HRR (2796 $kW.m^{-2}$) was recorded in the 365th second. The average HRR was 876 $kW.m^{-2}$. The ratio between the maximum and the average HRR was 3.19. In comparison, Martinka et al. [6] note a ratio of only 1.38 between the maximum and the average HRR for petrol. The difference between these values is due to the lower boiling point temperature of ETBE, in comparison to petrol. According to [22], the boiling point temperature of ETBE is 72 °C. However, petrol is a mixture of hydrocarbons with a different boiling point. According to [23], petrol shows a distillation residue of 72.6 % per volume at the temperature of 70 °C. Thus, approximately 72.6 % per volume of hydrocarbons comprising petrol boils at a temperature higher than ETBE. Beginning at approximately the 250th second, a rapid increase in HRR was caused by boiling (and the consequent rapid evaporation) ETBE. The heating of the tested ETBE up to its boiling point was further accelerated by the increasing depth level below the upper edge of the container.

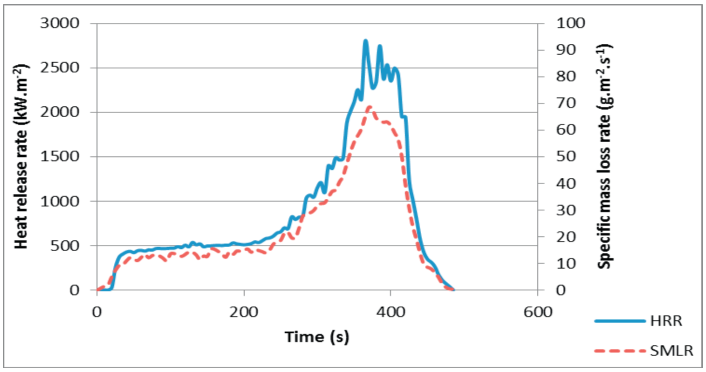

Fig. 1.Time dependent HRR and SMLR of ETBE unaffected by external heat radiation.

The specific CO production rate is shown in Fig. 2. The CO yield converted to sample weight loss was 10 $g.kg^{-1}$ and the CO yield converted to effective combustion heat was 0.41 $g.MJ^{-1}$. For comparison, according to Martinka et al. [6], the CO yield of petrol converted to weight loss was 58.6 $g.Kg^{-1}$ and, converted to effective combustion heat, it was 1.48 $g.MJ^{-1}$. The maximum HRR of petrol was nearly 850 $kW.m^{-2}$. Thus, given the test conditions, when compared with petrol, the fire hazard of ETBE was substantially higher regarding HRR but significantly lower regarding the CO yield.

The average SMLR for the entire duration of testing was 23.08 $g.m^{-2}.s^{-1}$. Within the 30 to 90 seconds time interval (interval following test commencement), the average SMLR was 11.83 $g.m^{-2}.s^{-1}$. Substituting the average SMLR (11.83 $g.m^{-2}.s^{-1}$), the pool diameter (0.106 m) and coefficient $k.\beta$ (the literature does not provide the coefficient for ETBE, therefore, the value for most chemically similar liquid, diethyl ether: 0.7 m^{-1} , was substituted – following [19]) into equation (1), the SMLR was calculated for ETBE burning in an infinite size pool (165.42 $g.m^{-2}.s^{-1}$). The calculated SMLR applies to ETBE burning in a container whose diameter is equal to or larger than 3.5 m (at this and larger diameter, the SMLR for ETBE during a pool fire is virtually constant – it does not increase with pool diameter).

Based on data measured, equations of linear statistical dependence of HRR (equation 2) and specific CO production rate (equation 3) on SMLR were compiled. The coefficients of determination R^2 for equations (2) and (3) were 0.9809 and 0.6311 respectively.

$$\mathrm{HRR} = 38.422 \cdot m''_{\infty} \tag{2}$$

$$\mathrm{SCPR} = 0.015 + m''_{\infty} \tag{3}$$

Where: HRR is the rate of heat release from an infinite size pool ETBE fire ($kW.m^{-2}$) and SCPR is the specific CO production rate from an infinite size pool ETBE fire ($g.m^{-2}.s^{-1}$).

Substituting m''_{∞}(165.42 $g.m^{-2}.s^{-1}$, calculated above), the HRR (6356 $kW.m^{-2}$) and the SCPR (2.57 $g.m^{-2}.s^{-1}$) were calculated from equations (2 and 3) valid for an infinite size pool ETBE fire. At SMLR 165.42 $g.m^{-2}.s^{-1}$, the calculated SCPR shows a 15.54 $g.kg^{-}$1CO yield.

Obtained results are realistic but there are still no other studies focused on bio-ETBE fire risks byinvestigation based on cone calorimeter method (oxygen consumption calorimetric method). Therefore, there are no other studies for compared with obtained results.

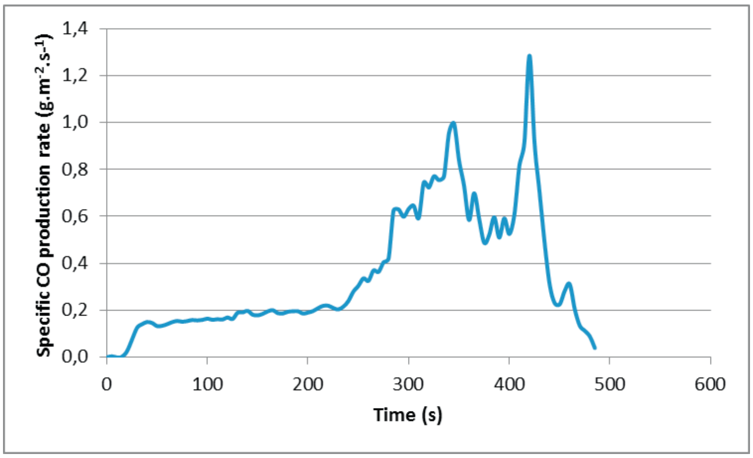

Fig. 2.Time dependent CO production rate of ETBE unaffected by external thermal radiation.

4. Conclusion

This article measured the HRR, SMLR and SCPR of ETBE using a cone calorimeter and a modified test procedure. The test procedure was modified in order to enable the investigation of flammable liquids. The average SMLR for the 30 to 90 seconds time interval, determined under test conditions, was converted by means of equation (1) into real conditions SMLR (pool diameter larger than 3.5 m) (165.42 $g.m^{-2}.s^{-1}$). Equations of linear statistical dependence of HRR and SCPR on SMLR were compiled from the obtained data. By substituting the SMLR calculated for an infinite size pool into the equations, the HRR (6356 $kW.m^{-2}$) and SCPR (2.57 $g.m^{-2}.s^{-1}$) were calculated for ETBE burning under the conditions of real pool fire (pool diameter above 3.5 m). At SMLR 165.42 $g.m^{-2}.s^{-1}$, the calculated SCPR shows a 15.54 $g.kg^{-1}$ CO yield.

Despite the fact that the obtained data is realistic and the HRR (6356 $kW.m^{-2}$), calculated by the above mentioned method, does not differ from HRR (5389 $kW.m^{-2}$) calculated on the basis of effective heat of combustion, SMLR, and 0.9 combustion efficiency (high combustion efficiency is indicated by a relatively low CO yield) by less than 20%, a high level of caution is advised when assessing the obtained data. There are two reasons for the caution with data assessment. First, the available literature does not provide the $k.\beta$ coefficient needed for the conversion of ETBE SMLR under test conditions into SMLR under conditions of real pool fire. Therefore, the coefficient was only estimated from values given for chemically similar liquids. The second reason is the fact that the precision of calculating SMLR for an infinite size pool from SMLR measured during a cone calorimeter test has been experimentally verified only for petrol in [6]. In spite of that, the obtained data will find important applications in evaluating fire risk by means of fire engineering tools. In the scientific studies [24-28] has been analysed this issue in great detail.

When juxtaposed to results provided by Martinka et al. [6], the obtained data further show a significantly higher combustion efficiency of ETBE (lower CO yield) in comparison to automobile petrol. This finding is particularly important for the field of environmental engineering. Therefore, the impact that amounts of bio-ETBE have, when mixed with petrol, on the combustion efficiency of the resulting mixture will be the subject of future research. The aim of future research will be finding optimal ratio of petrol and bio-ETBE for achievement the highest combustion efficiency of their mixture.

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References

[1]E. Planas-Cuchi, J.Casal, Flame temperature distribution in a pool fire, J. Hazard. Mater. 62 (1998) 231–241.
[2]M. Munoz, J. Arnaldos, J. Casal J, E.Planas, Analysis of the geometric and radiative characteristics of hydrocarbon pool fires. Combust Flame. 139 (2004) 263–277.
[3] A. Najafi, A.Z. Moghaddam, Modeling flame temperature profile on a fire-engulfed cylindrical tube, Flame Mater. 36 (2012) 565–574.
[4] V. Babrauskas, Ignition handbook, Fire Science Publishers, Issaquah, 2003.
[5] J. Martinka, E. Hroncová, T. Chrebet, K. Balog, A comparison of the behavior of spruce wood and polyolefins during the test on the cone calorimeter, Adv. Mater. Res. 726-731 (2012) 4280–4287.
[6] J. Martinka, T. Chrebet, K. Balog, An investigation of petrol fire risk bythe oxygen consumption calorimetry, J. Therm. Anal.Calorim. (2014) (ahead of print).
[7] A. Tewarson, F.H. Jiang, T. Morikawa, Ventilation-controlled combustion of polymers, Combust.Flame. 95 (1993) 151–169.
[8] J. Ladomerský, E. Hroncová, D. Samešová, Investigation of appropriate conditions for wood wastes combustion on basis of emission, Drew. 46 (2003) 90–98.
[9] M. Zachar, R. Skrovný, The influence of the radiant heat on the thermal degradation of specimens of spruce, ActaFacultatisXylologiae. 49 (2007) 61–68.
[10] J. Pitel, J. Mizak, Approximation of co/lambda biomass combustion dependence by artificial intelligence techniques, in: B. Katalinic (Ed.), Annals of DAAAM for 2011, DAAAM International, Vienna, 2011, pp. 143–144.

[11] I.S. Mulliqi, A.K. Terziqi, B.V. Barjaktari, A. MehushRifat, Impact of combustion time of lignite in the model of kinetic combustion in the boiler of Kosovo B, in: B. Katalinic (Ed.), Annals of DAAAM for 2011, DAAAM International, Vienna, 2011, pp. 825–826.
[12] P.V. Roslyakov, K.A. Pleshanov, I.L. Ionkin, Fuel combustion with monitored moderate underburning, in: B. Katalinic (Ed.), Annals of DAAAM for 2011, DAAAM International, Vienna, 2011, pp. 1153–1154.
[13] T.Chrebet, J. Martinka, I. Hrušovský, K. Balog,Monitoring of thermal degradation of fireproof coating, in: B. Katalinic (Ed.), Annals of DAAAM for 2012, DAAAM International, Vienna, 2012, pp. 1111–1114.
[14] J. Martinka, D. Kačíková, E. Hroncová, J. Ladomerský, Experimental determination of the effect of temperature and oxygen concentration on the production of birch wood main fire emissions, J. Therm. Anal.Calorim. 110 (2012) 193–198.
[15] J. Martinka, D. Balog, T. Chrebet, E. Hroncová, J. Dibdiaková, Effect of oxygen concentration on and temperature on ignition time of polypropylene, J. Therm. Anal. Calorim. 110 (2012) 485–487.
[16] M.G. Zabetakis, D.S. Burgess, Research on hazards associated with the production of and handling of liquid hydrogen, Bureau of Mines, Washington, 1961.
[17] B. Karlsson, J.G. Quintiere, Enclosure fire dynamics, CRC Press, London, 2000.
[18] D.T. Gottuk, D.A. White, Liquid fuel fires, in: P.J. DiNenno (Ed.), SFPE handbook of fire protection engineering, fourth ed., National Fire Protection Association, Quincy, 2002, pp. 297–316.
[19] V. Babrauskas, Pools, in: V. Babrauskas, S.J. Grayson (Eds.), Heat release in fires, Interscience Communications, London, 2009, pp. 201–206.
[20] ISO 5660-1:2002, Reaction-to-fire test-heat release, smoke production and mass loss rate, part 1 heat release rate (cone calorimeter method).
[21] Slovnaft, Ethyl tert-butyl ether A15400: product technical data sheet, Slovnaft, Bratislava, 2012.
[22] Efoa, Etbe: technical product bulletin, Efoa, Brussels, 2006.
[23] Slovnaft, Gasoline A100000: product technical data sheet, Slovnaft, Bratislava, 2012.
[24] A. Osvald, V. Mózer, Fire engineering a method for design fire safety, in: M. Zachar, K. Dúbravksá (Eds.), Proceedings of Advances in Fire and Safety Engineering, Technical University in Zvolen, Zvolen, 2012, pp. 211–223.
[25] V. Mózer, On equivalent fire exposure, Eur. J. Environ. Saf. Sci. 1 (2013) 18–23.
[26] S. Suard, S. Hostikka, J. Baccou, Sensitivity analysis of fire models using a fractional factorial design, FireSaf. J. 62 (2013) 115–124.
[27] A. Majlingová, M. Oravec, M. Šolc, Š. Galla, Modification of procedure to initiate the solids according to EN 60695-2-10 for materials used in historic buildings, Eur. J. Environ. Saf. Sci. 1 (2013) 8–12.
[28] Y. Wang, J. Jow, K. Su, J. Zhang, Development of the unsteady upward fire model to simulate polymer burning under UL94 vertical test conditions, Fire Saf. J. 54 (2012) 1–13.